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## EFFECT OF FLOW BREAKERS ON THE VUV PHOTOLYSIS OF AQUEOUS SOLUTION OF COUMARIN

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### Abstract

Vacuum ultraviolet (VUV) photolysis is one of the Advanced Oxidation Processes (AOPs) for the elimination of trace pollutants from water and air. During VUV photolysis reactive species (mainly  $\bullet\text{H}$  and  $\bullet\text{OH}$ ) can be generated directly from water without the addition of any chemicals. The penetration depth of VUV radiation in water is very small, only 0.04 mm, so reactive species form and react with organic compounds and dissolved  $\text{O}_2$  in this extremely thin layer. Carbon centered radicals can react at a longer distance from the light source, and their fast reaction with dissolved  $\text{O}_2$  results in an  $\text{O}_2$  poor layer, wider than the photo reaction zone. Consequently VUV irradiated solution is an extremely inhomogeneous system.

To reduce the inhomogeneity of the VUV irradiated aqueous solution flow breakers (PTFE rings) were used to enhance the mass transfer into the zone determined by the reactions of primary, carbon centered and peroxy radicals. Coumarin and its hydroxylated byproduct, the umbelliferone (7-hydroxy-coumarin) were used as model compounds. The effects of the PTFE rings on the transformation rate of coumarin and formation rate of umbelliferone were investigated in  $\text{O}_2$ -saturated and  $\text{O}_2$ -free solutions. The detailed investigation of the concentration effect of both dissolved  $\text{O}_2$  and coumarin is also reported in this work.

### Introduction

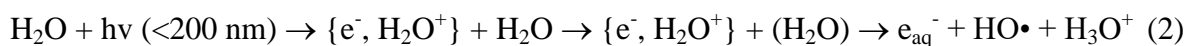
Advanced Oxidation Processes (AOPs) include chemical, photochemical, and electrochemical processes, based on the producing reactive species (especially  $\text{HO}\bullet$ ). These species can react with organic pollutants and possibly mineralize those in the presence of dissolved  $\text{O}_2$ . VUV photolysis, one of the AOPs, is based on high energy UV-radiation (wavelength  $<200$  nm). VUV light has enough energy to break the bound in water molecule and consequently produce  $\text{HO}\bullet$  and  $\text{H}\bullet$  reactive species.

Two typical VUV light sources exist. One of them is the low-pressure mercury vapour lamp, which emits both 254 nm UV and 185 nm VUV light. The other light source is the Xe excimer lamp, which emits quasi-monochromatic light with a wavelength maximum at 172 nm. There are several benefits of the excimer lamps, such as high average specific power radiation, high energy of emitting photons, quasi-monochromatic radiation, high spectral power density, absence of visible and IR radiation, low heating of radiating surface (cold lamps), no fixed geometry and no warm up time. [1]

In the case of 172 nm VUV radiation, the VUV irradiated zone is only 0.04 mm wide, because of the high molar absorbance of water at this wavelength. The primary reactive species ( $\text{HO}\bullet$ ,  $\text{H}\bullet$  and  $\text{e}_{\text{aq}}^-$ ), having a short lifetime, form and react within this zone.



$$\Phi(\text{HO}\bullet) = 0.42 [2,3]$$



$$\Phi(\text{e}_{\text{aq}}^-) = 0.045 - 0.05 [2,3]$$

The carbon centered radicals, which formed due to the reaction of organic pollutants with primary radicals, react fast with dissolved  $O_2$ . Because of the extremely high concentration of  $HO\bullet$ ,  $H\bullet$ , and carbon centered radicals, an  $O_2$  poor layer forms close to the wall of the light source. Thus the VUV irradiated solution can be characterized as an extremely inhomogeneous system, since both radical's concentration (primary and carbon centered radical) and dissolved  $O_2$  concentration decreases fast with the distance from the outside of the light source. [4].

The aim of this work was the investigation of the effect of flow parameters on the inhomogeneity of the zone characterized by  $O_2$  depletion and radical reactions. Coumarin was used as a model compound. According to the publications reported previously [5], the formation rate of umbelliferone, which is the hydroxylated product of coumarin, is proportional to the formation rate of  $HO\bullet$ .

### Experimental

The  $Xe_2^*$  excimer lamp (Radium Xeradex<sup>TM</sup>, 130 mm long, 46 mm diameter, 20 W) was centred in a high purity silica quartz envelope (53 mm diameter), which transmits the 172 nm light. The thickness of irradiated water layer was 5 mm. The aqueous solution was circulated continuously ( $375 \text{ mL min}^{-1}$ ) between the reactor and the liquid containing reservoir. Double walled, water cooled reactor was used and the temperature was set to  $25 \pm 0.5^\circ \text{C}$ . Samples were taken from the reservoir. The total volume of the circulated solution was 500 mL. The photon flux emitted by the excimer lamp (20 W) at  $172 \pm 14 \text{ nm}$  determined by methanol actinometry was found to be  $3.0 \times 10^{-6} \text{ mol}_{\text{photon}} \text{ s}^{-1}$  [6]. For investigation of the flow parameters 7 PTFE rings was placed into the reactor to break the laminar flow and increase the turbulence. These rings were 5 mm tall and 3 mm wide.

The transformation of coumarin was followed using spectrophotometry (Agilent 8453) at 277 nm. Fluorescence spectroscopy (Hitachi F4500) was applied to determine the concentration of umbelliferone. The wavelength of excitation was 387 nm, the determination of concentration was based on the intensity of the emitted fluorescence light at 455 nm.

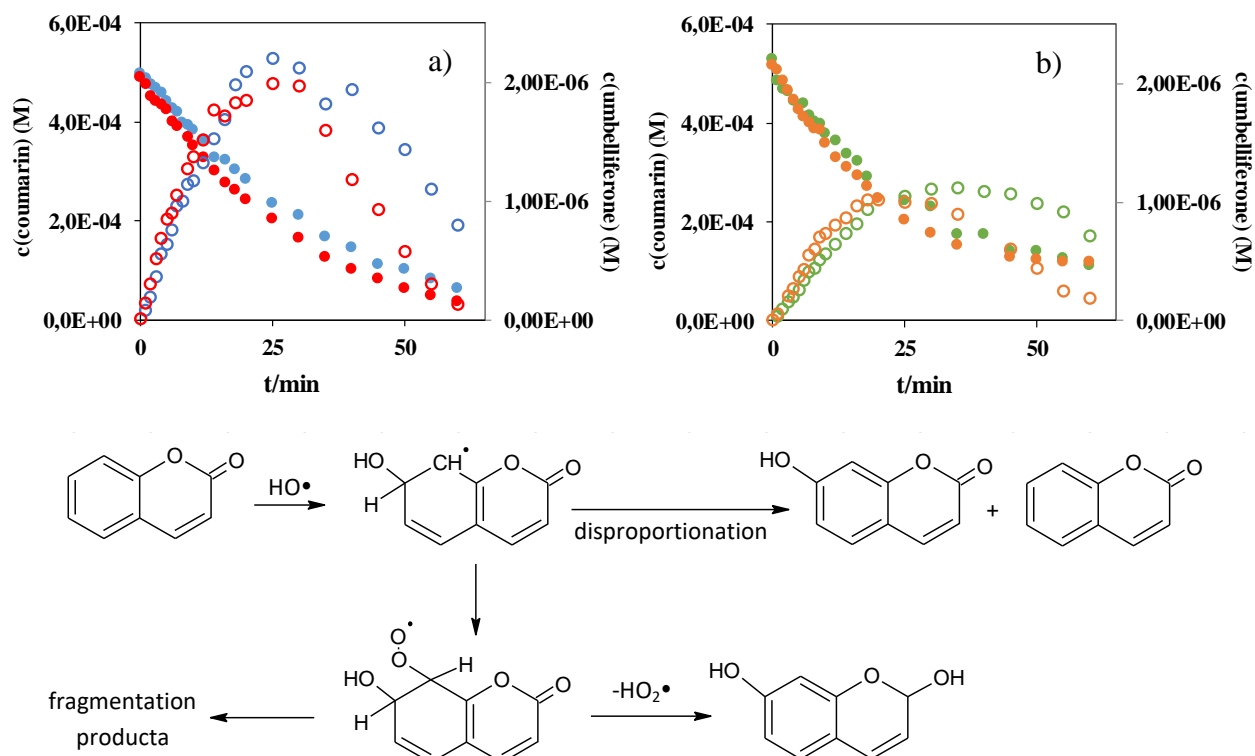
### Results and discussion

Dissolved  $O_2$  generally enhances the transformation rate of organic substances due to the formation of peroxy radical. The formation of peroxy radical opens up a new pathway for the further transformation of carbon centered radicals and hinders the backward reactions. In the case of VUV photolysis of aqueous solution, the formation rate of  $H\bullet$  is equal with the formation rate of  $HO\bullet$ . Moreover, rate constants of the reaction of coumarin with  $H\bullet$  ( $2.50 \times 10^9 \text{ M s}^{-1}$ ) and  $HO\bullet$  ( $6.88 \times 10^9 \text{ M s}^{-1}$ ) has similar values, thus both radicals can initiate the transformation with high rate. Dissolved  $O_2$  reacts with  $H\bullet$  and transform that into  $HO_2\bullet$  having very low reactivity [7]. In the case of 172 nm VUV irradiated  $5.0 \times 10^{-4} \text{ M}$  coumarin solution, there was no significant effect of  $O_2$  on the transformation rate, most probably because the positive effect (formation of peroxy radical) and negative effect (scavenging of reactive  $H\bullet$ ) of  $O_2$  compensate each other (Table 1 and Fig. 2.).

The reaction between coumarin and  $HO\bullet$  produce umbelliferone (7-hydroxy-coumarin). However the dissolved  $O_2$  has no significant effect on the transformation rate of coumarin, the formation rate of umbelliferone was about two times higher in the presence of  $O_2$  than in  $O_2$ -free solution. The formation of umbelliferone from coumarin is reported to be highly  $O_2$ -dependant: in the presence of dissolved  $O_2$ , umbelliferone forms via peroxy radicals, while in  $O_2$ -free solutions the hydroxylated products can be resulted only by the disproportionation and has lower yield [8] (Fig. 2). Consequently, the formation of umbelliferone requires  $HO\bullet$  initiated transformation of coumarin, while dissolved  $O_2$  highly enhances that via peroxy

radical formation. Transformation of coumarin and decomposition of umbelliferone take place parallel in the VUV irradiated solutions as Figure 1 shows that.

**Figure 1.** The concentration of coumarin and umbelliferone versus the time of irradiation in



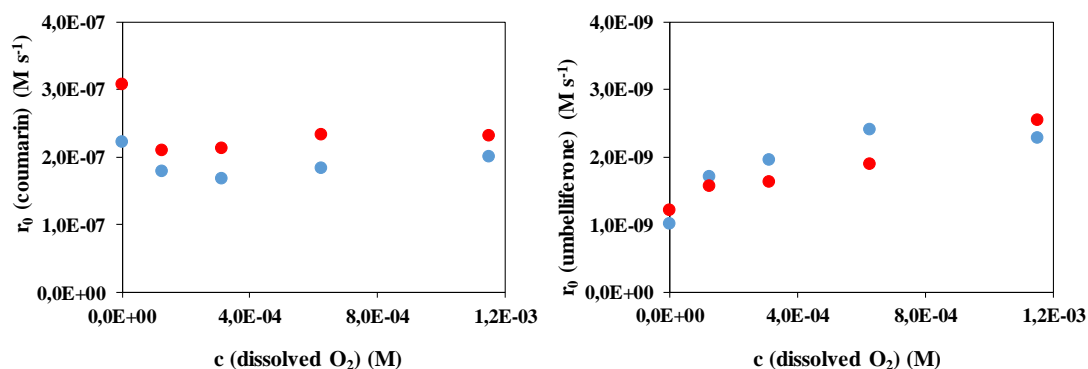
**Figure 2.** Formation of 7-HO-COU in the presence (a) and absence (b) of dissolved  $O_2$

For further investigation of the dissolved  $O_2$  effect, its concentration was changed between 0 and 100% in the gas flow bubbled through the solution. Thus the dissolved  $O_2$  concentration was changed between 0 and 40 mg dm<sup>-3</sup> in the aqueous solution. As Fig. 3 shows, the increase of  $O_2$  concentration in gas phase from 0 to 12% caused a slight decrease of the coumarin transformation rate. The further increase of  $O_2$  concentration slightly increased that. The effect of this factor is much more pronounced in the case of the formation of the hydroxylated product, umbelliferone. The formation rate of umbelliferone significantly increased when  $O_2$  concentration was changed from 0 to 50%. The further increase of  $O_2$  concentration has no effect.

**Table I.** Initial transformation rates determined at  $5.0 \times 10^{-4}$  M initial concentration of coumarin

	Initial transformation or formation rate	$O_2$ -saturated solution	$O_2$ -free solution
without PTFE rings	$r_0$ (coumarin) ( $\times 10^{-7}$ M s <sup>-1</sup> )	1.97	2.13
	$r_0$ (umbelliferone) ( $\times 10^{-9}$ M s <sup>-1</sup> )	2.27	0.93
with PTFE rings	$r_0$ (coumarin) ( $\times 10^{-7}$ M s <sup>-1</sup> )	2.87	3.12
	$r_0$ (umbelliferone) ( $\times 10^{-9}$ M s <sup>-1</sup> )	2.55	1.22

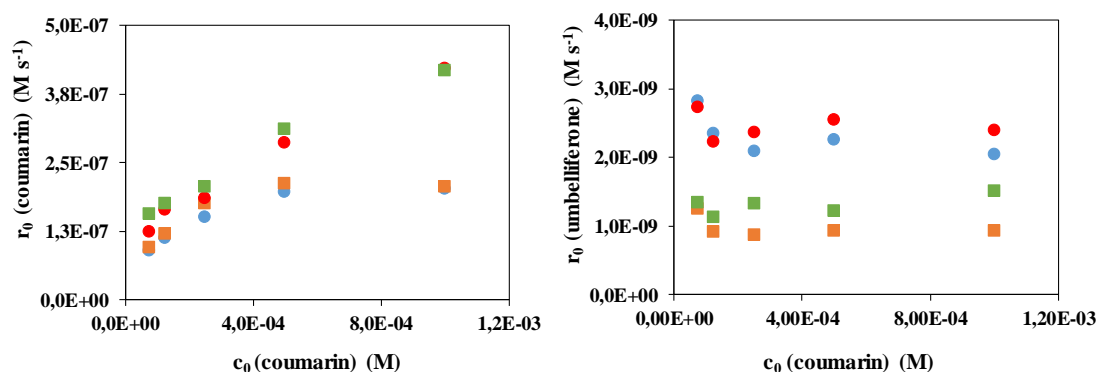
As that was mentioned previously, the VUV irradiated aqueous solution is a very inhomogeneous system: both  $\text{HO}\cdot$  and  $\text{H}\cdot$  concentration and dissolved  $\text{O}_2$  concentration strongly decreases with the distance from the wall of the light source. Installation of flow breakers (PTFE rings) in the reactor is aimed the breaking of this inhomogeneity via turbulence in the flow. As Fig. 3 shows, in the presence of PTFE rings higher transformation rate of coumarin was reached, mainly in  $\text{O}_2$ -free solution, when the increase was about 40%. Surprisingly the presence of  $\text{O}_2$  decreased the positive effect of the flow breakers.



**Figure 3.** The effect of dissolved  $\text{O}_2$  and PTFE rings on the transformation of coumarin ( $5.0 \times 10^{-4}$  M) and formation of umbelliferone

●: without PTFE rings; ●: with PTFE rings

The effect of flow breakers and dissolved  $\text{O}_2$  on the transformation rate of coumarin and formation rate of umbelliferone was investigated at various initial concentrations too. Since the transformation can be initiated by  $\text{H}\cdot$  and  $\text{HO}\cdot$ , the transformation rate of coumarin can be described by the following equation:  $r_{\text{cou}} = k_{\text{H}\cdot} \times [\text{H}\cdot] \times [\text{c}_{\text{cou}}] + k_{\text{HO}\cdot} \times [\text{HO}\cdot] \times [\text{c}_{\text{cou}}]$ . The value of  $[\text{H}\cdot]$  and  $[\text{HO}\cdot]$  is determined by the photon flux and quantum yield of their formation from water via absorption of 172 nm VUV light. The quantum yield is 0.42 for  $\text{H}\cdot$  and  $\text{HO}\cdot$  formation too. Moreover, as that was described previously,  $[\text{H}\cdot]$  is decreased by the dissolved  $\text{O}_2$ , which has to be taken into account. Thus the increase of the transformation rate with increase of the initial concentration of coumarin is expected. Above a given initial concentration, the transformation rate must be determined by the formation rate of primary radicals ( $\text{H}\cdot$  and  $\text{HO}\cdot$ ) and has to be independent on the coumarin concentration. As that was expected, at first the coumarin transformation rate increased with its initial concentration. Above  $5.0 \times 10^{-4}$  M, that was found to be independent on the coumarin concentration and determined by the formation rate of  $\text{H}\cdot$  and  $\text{HO}\cdot$  radicals. The positive effect of the flow breakers could be observed only in  $\text{O}_2$ -free solution and this effect was pronounced better with the increase of the coumarin concentration. Probably the PTFE rings are able to enhance the mass transfer into the zone determined by the reactions of various radicals, but not able to affect the primary radical and dissolved  $\text{O}_2$  concentrations in the VUV irradiated, very thin photoreaction zone. The latter supposition was confirmed by the fact that, the formation rate of hydroxylated product cannot be affected by the flow breakers.



**Figure 4.** The effect of initial concentration and PTFE rings on the transformation rate of coumarin and the formation rate of umbelliferone

●: without PTFE rings,  $O_2$ ; ●: with PTFE rings,  $O_2$ ; ■: with PTFE rings,  $N_2$ ; ■: without PTFE rings,  $N_2$

## Conclusion

- The presence of dissolved  $O_2$  increases the formation rate of umbelliferone, but there is no significant effect on the transformation rate of coumarin
- Flow breakers are able to increase the transformation rate of coumarin in  $O_2$ -free solution, but there is no effect on the formation rate of umbelliferone.

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## References

- [1] T. Alapi, K. Schrantz, E. Arany, Zs. Kozmér; Ed.: Mihaela I. Stefan, Advanced oxidation processes for water treatment : fundamentals and applications. IWA, 2018
- [2] G. Heit, A. Neuner, P.-Y. Saugy, A. M. Braun; J. Phys. Chem. A 1998, 102, 5551-5561
- [3] E. J. Hart, M. Anbar; Journal of Molecular Structure, 1970, 9, p. 486-486
- [4] S. Al-Gharabli, P. Engeßer, D. Gera, S. Klein, T. Oppenlander, Chemosphere, 2016, 144, 811-5
- [5] Y. Manevich, K. D. Heldt, John E. Biaglow. Radiation Research., 1997, 148, 580-591.
- [6] E. Arany, R. Szabó, L. Apáti, T. Alapi, I. Ilisz, P. Mazellier, A. Dombi, K. Schrantz, J Hazard Mater, 2013, 262, 151-7.
- [7] M. R. Gopakumar, K. Kini, U. R. Ashawa, S. C. Bhandari, N. S. Krishnan, G. U., Krishnan, D., Radiation Effects, 1977, 32, 199-203
- [8] G. Louita, S. Foley, J. Cabillic, H. Coffigny, F. Taran, A. Valleix, J. P. Renault, S. Pin, Radiation Physics and Chemistry, 2005, 72 (2-3), 119-124.